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AN EVALUATION OF HEAVY METALS IN SOME FRESH VEGETABLES AND SOIL SAMPLES IN THREE DIFFERENT CULTIVATED AREA OF TIRANA (ALBANIA)

P. LAZO, O. KATI, A. CABEJ and E. MARKU

Department of Chemistry, Faculty of Natural Sciences,
University of Tirana, TIRANA, ALBANIA
e-mail: veralazo@albmail.com

ABSTRACT

Three different cultivated area of Tirana region (315 ha altogether) where intensive chemicals have been applied for many years, were investigated for heavy metals contents (Cu, Cd, Pb, Zn, Fe, Ni, Co, Cr) in fresh vegetables (green salad, spinach, dill and parsley) and soil samples. Sixty vegetable samples (five of each kind of vegetables from each area) and sixty soil samples (collected in the same position with vegetable samples) were collected. Because agro-physical and chemical characteristics of these three areas are known by previous study and to decrease the standard error of the analysis, the soil samples of each area were mixed together. The same procedure was followed also for each kind of vegetable samples collected on the same area. It is found that the content of HM in all soil samples were not distinguished from the background level. Direct comparison and correlation procedures were used to evaluate the degree of contamination of vegetable samples of these areas. The content of HM in all vegetable samples investigated are within the allowed level.

Key words : Vegetable, Soils, Heavy metals, Background level, Index of geo-accumulation, Relative enrichment factor, Linear correlation factor

INTRODUCTION

Analytical investigation of heavy metals (Cu, Cd, Pb, Zn, Fe, Ni, Co, Cr) in fresh vegetables and soil samples from an area of 315 ha separated in three different cultivated areas with green salad, spinach, dill and parsley were done. Because the chemical and physical behavior of upper layer of cultivated soils are constantly modified by agricultural practices, it is reflected in the properties of some natural products, as vegetables were. Direct comparison and correlation procedures of HM were used to evaluate the degree of contamination of vegetable samples of these areas. The content of HM in all vegetable samples investigated are within the allowed level[1] and not higher than some normal levels published in other countries[2-7]

Some good correlation ($r > 95\%$) between the HM elements in vegetables and their content in soil samples of these areas were found. The HM content in dill and parsley samples found to be higher than in green salad and spinach samples, but not higher than allowed level of their content.

EXPERIMENTAL

Sampling procedure : Sixty vegetable samples (five of each kind of vegetables from each area) and sixty soil samples (collected in the same position with vegetable samples) were collected. Because agro-physical and chemical characteristics of these three areas are known[1,13] and to decrease the standard error of the analysis[7], the soil samples collected in the same area were mixed together. The same procedure was followed also for the samples of each kind of vegetables collected on the same area. Soil samples were collected 20 cm deep from the surface, air dried, sieved through a 2.0 mm screen, and then grounded and sieved through a 0.063 mm screen. The homogenized samples were stored in airtight pure plastic bags until used for chemical analyses. Twelve big samples of vegetables and twelve big soil samples were analyzed for HM content. Vegetable and soil samples were collected on the same day, in the same position.

Description of soil samples[12] : Soil forms the basis for plant production and thus performs a vital function in guaranteeing human survival. Soil quality consists in respect of its physico-chemical and biological condition. The stations under investigation, Selita (St 1), Fushe Preza (St 2) and Kashar (St 3), positioned in the west part of Albania (north part of Tirana) in an altitude of about 200 m, with Mediterranean hilly climate, with an average yearly temperature of about 15-21°C and average yearly raining of about 1300-1800 mm. These are classified as alluvional hilly soils (brown reddish sands). Asphodelius microcarpa Brot is there most important plant. Their appear weak acid reaction with a pH value varying from 5.2 to 5.4. They participate on heavy sub clayey lands and are classified as argil-sandy formation. The content of humus is 1.5-2.3% and of nitrogen is 0.15-0.2%. The content of heavy metals is given in Table 1[13].

Table 1. HM content in soil samples[13] (mg/kg in dry weight)

Station	Cu	Pb	Ni	Co	Cr	Zn	Fe*1000	Mn
St.1	25-80	30-90	80-300	5-35	50-120	80-150	26-38	500-800
St.2	10-50	20-60	80-250	10-40	50-120	40-100	15-25	500-1500
St.3	25-80	10-30	120-350	10-40	60-200	80-130	33-48	500-800

* Two different deepness from the surface are used for soil samples collecting; 5 cm and 40 cm deep

The content of heavy metals in these areas is within normal level[1] for vegetable cultivated area. These elements are important for the plant in normal concentration, and became dangerous in surplus content[14], so the examination of HM content periodically is very important. For example, trivalent chromium is an important trace element for humans and animals in the insulin metabolism, or Ni is an important trace element for plant growth, but a surplus of Co results in a Fe and Cu deficit. On other hand, lead has a toxic effect on growth. It inhibits the intake of essential nutrients from the soil, while Zn inhibited growth of the plant[1].

Methods of chemical analysis : Whole sample digestion procedure was used. Flame atomic absorption spectroscopy was used for Zn and Fe determination[9, 8]; furnace electro thermal system was used for all other HM metals[9, 10] (except Cr) determined via Varian AA-10 Plus AAS. Cr was determined as Cr^{6+} after complex formation with biphenyl carbazide using SF UV-VIS method[11].

RESULTS AND DISCUSSION

Experimental results of mean concentration values of HM elements in soils and vegetables samples are summarized in Tables 2 and 4.

Table 2 HM content in soil samples (mg/kg in dry weight)

Station	Cu	Pb	Ni	Co	Cr	Zn	Fe*1000	Mn
St.1	61.9	92.5	249.5	25.00	100.5	177.8	39.2	904.5
St.2	33.0	43.8	183.8	20.20	67.0	71.2	24.7	1214.5
St.3	67.5	16.5	344.8	36.35	112.8	129.6	46.8	935.5

The Index of Geoaccumulation[15], (C_n represents metal concentration and B_n represents background concentration of the same element) was calculated for each heavy metal. The minimum values of HM elements given in Table 1 were used as background level. The classification of elements according to their I_{Geo} level is given in Table 3.

Table 3 The classification of HM elements according to I_{Geo}

Elements	Cu	Pb	Ni	Co	Cr	Zn	Fe	Mn
I_{Geo} St 1	2.04	1.62	1.06	0.74	0.42	1.57	0.8	0.27
St. 2	1.14	0.55	0.62	0.45	0.16	0.25	0.13	0.69
St. 3	2.17	0.86	1.52	1.28	0.59	1.11	1.056	0.32

Station 2 presents the lowest values of I_{Geo} for all HM elements. Only Cu presents $I_{Geo}\approx 2$ in stations 2 and 3, Pb, Ni and Zn present $I_{Geo}\approx 1\text{-}1.6$ in station 1, Fe, Co, Ni and Zn present $I_{Geo}\approx 1.1\text{-}1.6$ in station 3. For the remaining elements present $I_{Geo} < 0$, which mean the content of these elements were not distinguished from the background level, B_n. The relative enrichment factor (RE = (C_{HM} / C_{Fe}) sample / (C_{HM} / C_{Fe}) background) was calculated, too. The calculated values of RE factors were found to be smaller than zero for all elements, so HM elements did not present any significant enrichment in these areas.

From the results of Table 4, it is shown the content of HM in all vegetable samples were within the allowed level[1], or within the range of other publications in other countries[2-7]. It was found that dill and spinach are rich with most of elements; but the contents of each element in each vegetable sample collected on different station do not differ significantly from each other.

Table 4 HM content in vegetable samples (mg/kg in dry weight)

Sample/station		Cu	Pb	Ni	Co	Cr	Zn	Fe	Mn
Dill	St. 1	4.39	0.23	0.37	0.66	0.00	39.73	248.5	29.80
	St. 2	9.90	0.45	0.51	1.68	0.00	119.25	188.8	29.80
	St. 3	6.21	0.21	0.46	1.00	0.00	39.65	248.3	39.65
Parsley	St. 1	4.70	0.28	0.80	0.52	4.17	39.85	289.5	29.95
	St. 2	4.78	0.37	0.68	1.05	4.20	49.50	242.8	38.35
	St. 3	10.22	0.37	0.99	0.56	8.38	39.85	279.0	29.90
Green Salad	St. 1	11.20	0.68	0.16	0.66	1.26	39.90	149.4	59.75
	St. 2	8.00	1.15	0.15	1.05	8.38	66.55	139.4	29.80
	St. 3	7.57	0.86	0.39	0.74	16.80	29.90	59.9	36.50
Spinach	St. 1	7.08	1.14	0.29	1.71	4.20	29.90	239.4	39.84
	St. 2	7.64	0.21	0.54	1.33	4.20	67.85	271.5	19.35
	St. 3	6.60	0.85	0.31	1.09	0.00	38.80	229.0	39.8

Linear correlation coefficient between elements in vegetables samples was calculated. Positive significant correlation ($r \approx > 0.6$) was found for Fe-Ni, and negative significant correlation ($r \approx > -0.6$) was found for Ni-Pb, Fe-Cr (see Table 5) in vegetable samples, which mean Fe and Ni are imperatival elements and Pb replace Ni or Cr replace Fe during accumulation of these elements from these plants.

Table 5. Linear correlation coefficients between elements in vegetables samples

	Cu	Pb	Ni	Co	Cr	Zn	Fe	Mn
Cu	1							
Pb	0.2551	1						
Ni	- 0.1209	- 0.6318	1					
Co	0.1136	0.3017	- 0.2875	1				
Cr	0.4493	0.4013	- 0.1217	- 0.3979	1			
Zn	0.3336	- 0.1448	0.0166	0.5408	- 0.3209	1		
Fe	-0.3745	- 0.5932	0.5955	0.0144	- 0.6864	- 0.0533	1	
Mn	0.3001	0.19823	- 0.3856	- 0.3416	0.3954	- 0.3348	- 0.4569	1

All the elements in all samples under investigation have a positive significant correlation (r>0.75) between HM content in vegetables and soils samples (Table 6), so we can achieve a conclusion that the main source of these elements in vegetable samples were from the soils.

Table 6. Linear correlation coefficients of total HM elements between vegetables and soil samples

Sample/Station	Station 1	Station 2	Station 3
Dill	0.985315	0.822909	0.984005
Parsley	0.989846	0.977531	0.989261
Green salad	0.915082	0.892385	0.751679
Spinach	0.990349	0.970183	0.977591

CONCLUSION

The values of index of geo-accumulation of heavy metals (HM) and relative enrichment factor obtained for soil samples under investigation mean the content of heavy metals in these areas were not significantly distinguished from background level. It is near background allowed level, which is reflected to the content of heavy metals in the plants under investigation.

The content of HM in all vegetable samples investigated were within the allowed level. It was found there were not significant differences between HM content in dill, parsley, and spinach and green salad samples collected in three different area of Tirana.

Positive significant correlation ($r \approx > 0.6$) was found for Fe-Ni, so we can say that these elements are essentials for these plants. Positive significant correlation ($r > 0.75$) between vegetable and soil samples for all elements, show that the main source of these elements in these vegetable samples were from the soils of the cultivated area.

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